A SANS study of organo-clay dispersions [1, 2]

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ABSTRACT

Small angle neutron scattering (SANS) is used to investigate the dispersion in toluene of various forms of the complex, Cloisite C15A. Cloisite is a commercially important exchanged clay prepared from montmorillonite and the cation di-tallow ammonium. Points discussed include estimates of the extent to which the complex is dispersed, the amount of organic clay platelet surface layer coverage, and possible network formation of the complex in the solvent. From power law plots of the scattered neutron intensity verses the wave vector, we estimated that C15A is well dispersed into clusters which consist of a stack of about 12 di-tallow coated montmorillonite platelets. Removing excess di-tallow from the surface layer reduces the cluster size. Substituting dimethydioctodecyl ammonium for di-tallow molecule promotes network formation. We demonstrate that, in general, SANS is a powerful tool by which to examine these complicated organic/inorganic systems.

KEY WORDS: clay nanomaterial; Cloisite 15A; clusters; dispersions; di-tallow; gel; montmorillonite; organic/inorganic complex; small angle neutron scattering (SANS).

1. INTRODUCTION

As is very well known, a typical polymer/clay nanocomposite is composed of a filler embedded in a polymerized medium [1]. The filler is an organo-clay, usually a cationic complex in which the clay's natural surface metal cations have been exchanged with an organic, cationic surfactant. The surfactant layer is organophilic allowing the inorganic clay to be dispersed in the organic polymer. As is also well known, the mechanical and thermal characteristics of the nanocomposite itself depend largely on the degree to which this dispersion can take place. Optimum characteristics occur when the largest possible clay surface area is made available for cation exchange, when this surface area is maintained throughout the exchange process, and when it is maintained during the subsequent polymerization. Ideally, then, the clay mineral should be separated into its constituent platelets in the nanocomposite precursor state.

Small angle neutron scattering (SANS) is an excellent tool to probe the degree of separation or dispersion of an exchanged clay mineral in a solvent, as several authors have demonstrated. Published results to date, however, seem to be restricted to complexes in an aqueous medium [2]; a surprising limitation considering that organically based systems are industrially the more important and wide spread. But, very recently, we reported [3] the behavior of the standard commercial complex known as Cloisite C15A in toluene. Cloisite is the material prepared from montmorillonite and the cation di-tallow (a naturally occuring variant of dimethydioctodecyl ammonium).

The results of [3] relevant here were as follows. First, that the complex is well dispersed in toluene in that it forms clusters made up of a stack of between about 6 and 12 di-tallow coated montmorillonite platelets. The SANS data, reinforced by dynamic light scattering estimates of the hydrodynamic particle size, and by data from wide angle x-ray scattering, indicated that the diameter of the major face of a C15A cluster is about 260 nm, and its height is between approximately 25 and 55 nm. Second, it was clear that small changes in the extent and nature of the clay platelet surface coverage played potentially a key

role in the dispersion mechanism. This point is followed up in this paper. As in reference [3], our samples were 1% and 2% suspensions of Cloisite C15A in toluene, but the study reported in [3] is extended. Commercial Cloisite has an excess of surfactant di-tallow associated with a montmorillonite clay platelet. (Excess being defined as an amount exceeding the cation exchange capacity, CEC, of the montmorillonite.) Here we: a) investigated the dispersion and behavior of complexes prepared from pure di-tallow with any excess di-tallow removed (designated 'pure di-tallow'); b) investigated the system when the di-tallow is replaced by its pure synthetic counterpart, dimethydioctodecyl ammonium (designated '2C18') Our overall objective is to see if the information thus gained will allow us to understand better aggregation and dispersion of complexes in organic solvents and in small organic molecules in general (e.g. organic oligomers used as epoxy/thermoset precursors).

2. MEASUREMENTS

2.1. Materials.

The clay materials used in this work were C15A, its variants, and the sodium montmorillonite base, designated CNa+. C15A and CNa+ are commercial products provided to us as powders by Southern Clay Products, Inc.[4]. The supplier synthesized C15A by exchanging the sodium ions of CNa+ with 125 meq/100g of the di-tallow. The di-tallow itself is a mixture of dimethyl ammonium surfactants with various carbon chain lengths: C_{18} (65%), C_{16} (30%) and C_{14} (5%). The CEC of CNa+ is estimated to be 92 meq/100g. Hence the surface of C15A is covered to about 130% of one CEC layer.

A nominal 1% by weight dispersion of CNa+ was made up by adding the commercial powder to distilled water and stirring vigorously for 3 hours. This dispersion was then sonicated for 20 mins and lightly centrifuged for 5 mins. The elluent was a clear and stable suspension. This suspension was then diluted to give two other dispersions of nominal 0.5% and 0.1% by weight clay content, respectively.

1% and 2% by weight suspensions of C15A in toluene were prepared following the simple procedure recommended by the supplier. For example, for a 2% suspension: 1g of C15A was added to 57.7 mls of toluene and the solution stirred for 30 mins in a flask. At this point 0.379 mls (30% of the clay content, ie., 0.3 g) of methanol and 0.2 mls of water were added, and the mixture stirred for a further 30 mins. On occasion some samples were also sonicated briefly. We observed that the suspension was clear and stable for several weeks with no significant settling. The suspension was, however, very viscous. The 1% suspension was made up by direct weighing, and also by dilution of the 2% stock. The procedures were repeated with d-toluene, and with mixtures of d- and h- toluene as the solvent. The results here are reported for a 50/50 d/h toluene mixture.

Pure di-tallow was provided by Rheox [4] and dimethydioctodecyl ammonium chloride was purchased from Aldrich [4]. The complexes were prepared by cation exchanging the commercial CNa+ with these pure surfactants. Excess surfactant was subsequently removed by refluxing with methanol for 3 days. The 1% and 2% by weight solutions of these materials in toluene were prepared by the procedure outlined for C15A. It turned out that the pure di-tallow suspensions were viscous and tended to gel; the gel could only be broken by sonification. The 2C18 systems were, however, gel like throughout, and a fluid suspension was not obtainable.

2.2 Neutron scattering.

Neutron scattering intensities from the CNa+ clay and the complex suspensions were obtained from the appropriate samples loaded in 1 mm gap-thickness quartz cells and placed in the beam of the 30 m NG7 SANS instrument at the National Institute of Standards and Technology Center for Neutron Research (NCNR). The spectrometer was configured with an incident neutron wave length λ = 0.6 nm and sample-detector distances of 1.2 m, 5.0m and 15.3m to give a wavevector range 0.02 < q nm^{-1} < 1.2. Here $q = |\mathbf{q}|$ and $q = 4\pi \sin(\theta/2)/\lambda$, with λ the incident neutron wave length and θ the scattering angle. Scattered neutrons were detected on the instrument's 2D position sensitive detector. Because

all measured scattering patterns were isotropic, the measured counts were azimuthally averaged. These averaged data were corrected for empty cell and solvent scattering in the usual way and were placed on an absolute scale by normalizing to the intensity obtained from a water standard [5].

2.3. Small angle neutron scattering equations.

The coherent contribution to the scattered intensity $I(q)$ from a monodisperse suspension of N particles of volume V_p occupying volume V is proportional to the differential cross section per unit volume of the sample $d\Sigma/d\Omega$ (cm^{-1}) [6, 7]:

$$d\Sigma/d\Omega = (N/V)|F(\mathbf{q})|^2 S(\mathbf{q}) \quad . \tag{1}$$

This equation expresses the total coherent scattering in terms of a single particle form factor

$$F(\mathbf{q}) = \sum_j b_j \exp(i\mathbf{q}\cdot\mathbf{X}_j) \tag{2}$$

and the structure factor, $S(\mathbf{q})$ which accounts for interparticle interference. The term b_j in Eq.(2) is the neutron scattering length of nucleus j. One, however, often considers the scattering length density defined operationally by $\rho = \rho_{mol}\sum b_j N(j)$, where ρ_{mol} is the molecular density and $N(j)$ is the number of nuclei of type j in a particle.

Experimentally, scattering from a species is measured with respect to the scattering length density of the medium ρ_m. If this scattering length density difference is independent of particle position, the cross section, and hence the scattered intensity, for an isotropic, non-interacting system can be written in terms of the volume fraction ϕ, where $\phi = (N/V)V_p$:

$$I(q) = A\phi V_p(\rho - \rho_m)^2 P(q) \tag{3}$$

where A is an apparatus constant. $P(q)$ is the square of the orientationally averaged $F(\mathbf{q})$ written in dimensionless form: a term that can be evaluated analytically if the geometry of the scatterers is known. Here we will assume that the clay platelets can be approximated by disks and, for a disk of radius R and height $2H$, we have:

$$P(q) = 4\int_0^{\pi/2}\left(\frac{\sin^2(qH\cos\beta)}{(qH)^2\cos^2\beta}\right)\frac{J_1^2(qR\sin\beta)}{(qR)^2\sin^2\beta}\sin\beta d\beta \qquad (4)$$

where J_1 is the first integer-order Bessel function and β is the angle between $\mathbf{q}$ and the major axis of the disk. Equation (7) simplifies considerably if $qH << 1$. In this case the first term in the integral is equal to 1 so that Eq.(4) becomes

$$P(q) = \frac{2}{(qR)^2}\left[1 - \frac{J_1(2qR)}{qR}\right] \quad . \qquad (5)$$

For qR >2 the asymptotic formula

$$P(q) = \frac{2}{(qR)^2}\exp[-(qH)^2/3] \quad . \qquad (6)$$

is a useful approximation. The equations imply that a plot of Log (I) verses Log (q) from a system of non interacting disks will have a slope of -2 over a range of qR.

In this work, the scatterers are clay platelets for which the surface sodium ions have been replaced by an organic interface, and the organo-clay complex can be considered as made up of a central core and a surface coating. If this core has a characteristic scattering length density ρ_1 and the surface has a characteristic scattering length density ρ_2, the

scattered intensity from a system of isolated particles is of the form

$$I \sim \left\{(\rho_2 - \rho_m)\left[V_T P_T(q) - V_1 P_1(q)\right] + (\rho_1 - \rho_m) V_1 P_1(q)\right\}^2 \qquad (7)$$

where V_1 is the volume of the core, and V_T the total volume of the particle.

Inspection of Eq. (7) indicates that if the scattering length density of the medium is the same as that for the surface species 2, the SANS intensity pattern will be from the core. Similarly, if $\rho_1 = \rho_m$ the scattering power of the system is controlled by the surface.

Scattering lengths and scattering length densities, together with the molecular mass and the mass density of the components of the suspensions are listed in Table 1. The parameters for CNa+ are those for a clay mineral layer with the formula $\left[Si_4Mg_{0.33}Al_{1.67}H_2O_{12}\right]Na^+_{0.33}$. The parameters for the di-tallow assume the carbon chain breakdown discussed above, namely C_{18} (65%), C_{16} (30%) and C_{14} (5%).

Table 1. Parameters for the CNa+ and the complex systems.

	molecular mass	mass density	scattering length	scattering length density
	g	g cm^{-3}	10^{-12} cm	10^{10} cm^{-2}
CNa+	359.4	2.66	8.647	3.86
di-tallow+	545.6	0.9	-3.58	-0.35
di-tallow Cl	581.1	0.9	-2.62	-0.24
di-C_{18}	550.0	0.9	-3.71	-0.36
toluene	92.0	0.867	1.665	0.90
d-toluene	100.0	0.943	9.991	5.68
H_2O	18.0	1.0	-0.168	-0.56

3. RESULTS AND DISCUSSION

3.1 Montmorillonite, CNa+

We refer to reference [3] for a discussion on the SANS intensities measured from an 0.5% suspension of CNa+ in water. The power law slope of the curve *I(q)* vs. *q* was -2.2: a result consistent with the predictions of Eqs. (4) to (6), given that the sample is estimated by the manufacturer to be 20-30% polydisperse. The SANS data thus suggest that the unexchanged clay sample forms suspension of non interacting thin platelets. As also reported in [3] these SANS data, together with results from dynamic light scattering, indicate that 2R is approximately 260 nm; wide angle x-ray data indicate that H is approximately 1 nm.

3.2 Commercial Cloisite C15A

Small angle neutron scattering measurements were carried out on the 1% and 2% C15A samples in two solvents. The first set of SANS data were obtained with the Cloisite suspended in toluene. Scattering from the di-tallow is not contrasted out, but is minor compared to that from the CNa+ core. The second set were obtained from a 50/50 d/h-toluene suspension. Here the scattering length density of the solvent almost matches that of the core, so the scattered intensity is essentially that from the surfactant layer alone. The SANS intensity patterns for the 1% and 2% C15A systems are given in [3]. The result for the 2% sample is reproduced here.

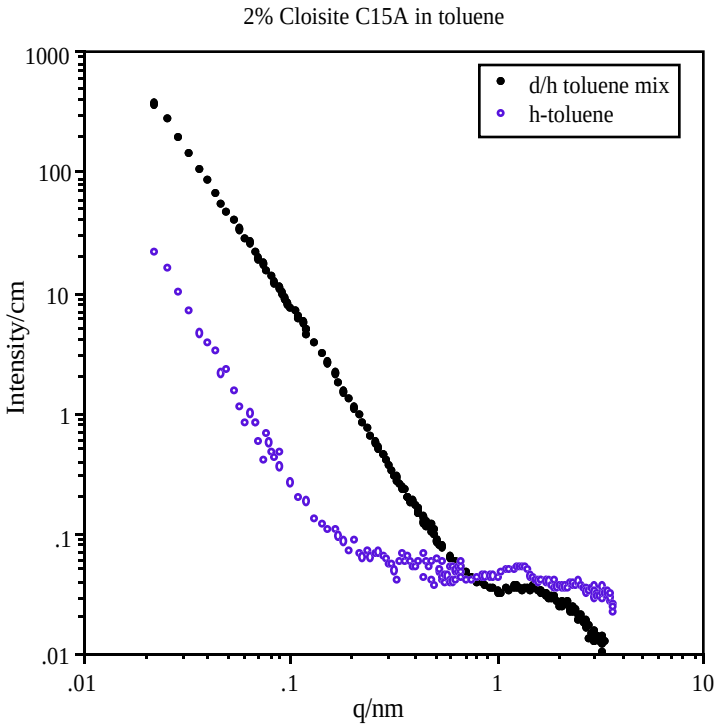

Figure 1. Scattered intensities from a 2% suspension of Cloisite C15A in toluene.

It is seen that the scattering from the suspensions in d/h-toluene displays power law behavior over a wide range of the wave vector with a slope of -2.5, slightly more negative than the slope of -2.2 associated with CNa+. Note that the curves show definite structure at q >1.0 nm^{-1}, absent in the corresponding plot for CNa+. Not shown are the very similar curves for the 1% suspension only, in this case, the slope is slightly more negative at -2.9 [3].

Wide angle x-ray scattering experiments were carried out to investigate the SANS evidence of structure at the higher values of *q* [3]. The complex C15A was investigated dry, that is as supplied by Southern Clay products, and as 1% and 2% suspensions in the toluene solvent. Evidence of three orders of primary spacing of about 4.5 nm was observed. Since

the d-spacing between dry CNA+ was measured to be 0.99 nm, 4.5 nm corresponds to a single di-tallow layer thickness of about 1.75 nm.

Overall, the x-ray data compliment the SANS data. We believe that the intensity curves, especially the curves that contrast out the clay core, indicate that the disk like structure of the CNa+ platelets is preserved in the complex, only that the C15A disk is made up of several stacked platelets. Taking into account that the complex suspensions are 20-30% polydisperse, we can estimate from Eq. (4) that slopes of -2.5 and -2.9 would be generated from a disk of height H between about 10% and 20% of the radius R. Given that we have shown that 2R for CNa+ is about 260 nm, the thickness of the C15A complex is thus approximately 26 nm and 52 nm for the 2% and 1% systems, respectively. Given the x-ray data, this suggests that the C15A clusters in the 2% suspension are stacks of about 6 exchanged clay platelets, and in the 1% suspension, stacks of about 12 exchanged platelets.

A method, introduced by Hanley *et al* [2] that requires no assumptions on the surface morphology, gives an estimate of surface coverage. A shift in the forward scattering for a sample in various solvents is proportional to the number of mols displaced by the scatterers. The scattering power of, say, one mole of scatterer *a* that displaces x_{ab} moles of solvent *b*, Δ_{ab} is

$$\Delta_{ab} = \left[\sum_{ia} b_i - x_{ab} \sum_{ib} b_i \right]^2 \qquad (8)$$

Supposing one mole of scatterer *a* now has x_c moles of a surface compound *c* attached to it, and species *c* displaces x_{cb} moles of solvent *b*. The scattering power then becomes

$$\Delta_{acb} = \left[\left(\sum_{ia} b_i + x_c \sum_{ic} b_i \right) - \sum_{ib} b_i \left(x_{ab} + x_{cb} \right) \right]^2 \qquad (9)$$

In our case, the unknown quantity is x_c, the number of moles of di-tallow that form the surface layer of one mol of CNa+. But this can be estimated from the ratio of the

scattering power of C15A in the two solvents, toluene and d/h- toluene. If we assume that the surface layer is one CEC equivalent of di-tallow+, Eq. (9) predicts a ratio between the scattered intensities from the sample in toluene and the 50% d/h-toluene mixture of approximately 20. The experimental ratio for the 2% suspension is around 25 (Figure 1) but, for the 1% suspensions [3], the value is much higher at ~ 60. If, however, we realize that the surface layer contains some di-tallow molecules (ie., with Cl), the ratio calculated from Eq. (11), increases substantially. Specifically, if 0.1 moles of di-tallow is in excess (based on the suppliers estimate that the surface of dry C15A is covered to about 130% of one CEC layer) the ratio is about 120. It is thus reasonable to assume that the surface of the suspended C15A does contain excess di-tallow, but that the excess is greater on the 1% complex.

It turns out that the 2% suspension is much the more viscous. Hence the SANS calculation reinforces strongly the argument that the amount of excess surfactant plays a very significant role in both the platelet cluster formation itself and in the network or gel like characteristics of the suspension on a longer length scale.

SANS data for the pure di-tallow dispersions are displayed in figure 2. The slopes from the curves obtained in d/h toluene are -2.5 for both the 1% and 2% dispersions. Some structure at the higher q is evident, as seen in figure 1.

For the 1% suspension, the displacement calculation method is consistent with the fact that the surface coverage is limited to one CEC since the complexes were washed free of excess surfactant. In figure 2 the curves from the 2% sample in toluene deviate slightly from a parallel pattern at low-q. Moreover, the displacement method gives an unrealistically low surface coverage estimate for this sample leading us to conclude that the assumption that the complexes are behaving as non interacting particles in the solvent (ie., that the structure factor $S(q)$ is no longer unity for all q) is invalid. Deviations from general power law behavior are more apparent in the intensity patterns from the 2C18 suspensions, figure 3. It is very clear that, while the curves from the complex in d/h toluene suspension follow power law behavior with slopes of -2.5, the curves for the complex in toluene display a rise at the

lower *q*, and are definitely suggestive of complex-complex interaction. It is straightforward

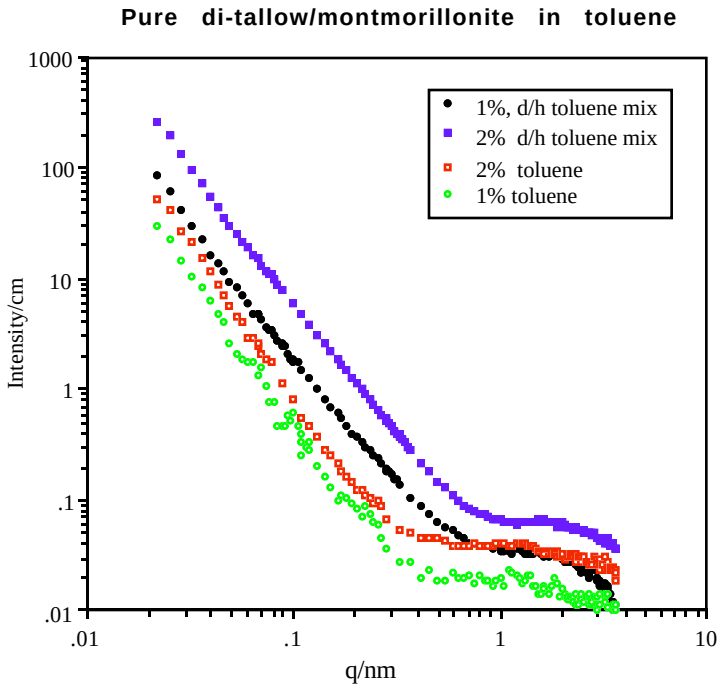

Figure 2. SANS intensities from the complex prepared from pure di-tallow in toluene.

to estimate the structure factor. The intensities from the sample in d/h toluene depict scattering from the surface layer and approximate the form factor of a disk. Hence an effective *S(q)* follows immediately from Eq. (1), figure 4. The plot shows a substantial rise at low *q*, which, in our opinion, indicates a length in the system of at least 200 nm. There is also evidence of a peak at about $q = 0.27$ nm^{-1}, which indicates a length of the order of 25 nm.

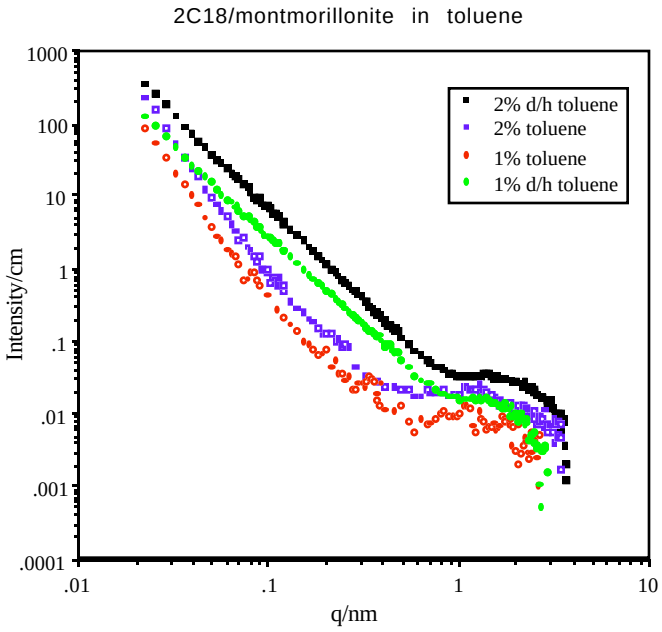

Figure 3. SANS intensities from the complex prepared from 2C18 in toluene.

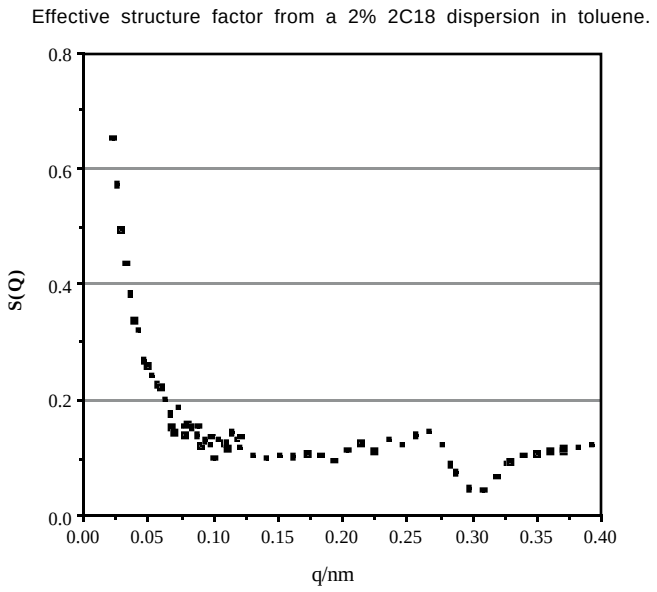

Figure 4. Effective structure factor of 2% 2C18 in toluene.

CONCLUSION

We considered three variants of the organically modified montmorillonite (Cloisite) suspended in toluene: the commercial product that contains excess surfactant, a complex prepared with pure di-tallow and free of excess surfactant; and the complex prepared from dimethydioctodecyl ammonium chloride. The SANS data reported in this paper, and in [3], indicate that the clay platelets of these various Cloisites can be dispersed in toluene, only that the platelets aggregate to form small clusters. Nevertheless, the aggregate has a disk shape with a very high aspect ratio, so that a large amount of the exchanged surface area is available.

An objective of this work was to see how modifying the surfactant surface layer of the exchanged clay might affect the dispersion. The power law $I(q)$ vs, q curves indicate that washing, purifying, and/or slightly changing the chemical make up of the surfactant, does

reduce slightly the cluster size compared to that observed from the unmodified commercial product. This observation is confirmed by the behavior of the SANS data at higher *q*, figure 5. A peak from C15A at around $q = 1.2$ nm^{-1} (also observed from wide angle x-rays [3]) which represents the internal platelet spacing within the cluster is very apparent This peak is subdued in the curves obtained from the pure di-tallow and the 2C18, however. We have indeed demonstrated that the exchanged clay may thus be slightly more exfoliated by changing the nature of the surfactant layer, but the potential for gelation is increased.

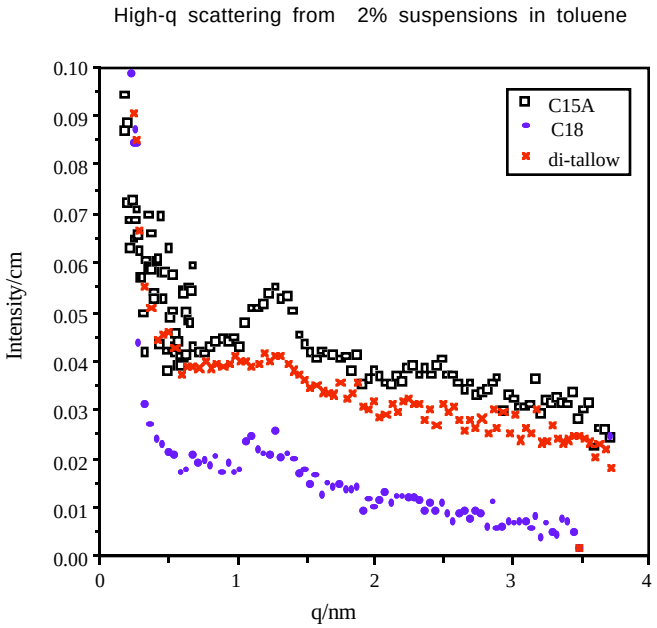

Figure 5. SANS curves emphasizing the high q pattern from the three Cloisites in 2% toluene.

We conclude this paper with our concept of the structure of this gel. The SANS 2C18 data suggest four characteristic lengths: the internal radius and height of the cluster

and, as seen in figure 4, two cluster-cluster interaction lengths of about 25 nm and > 200 nm. The results from the d/h toluene sample (ie., scattered intensities of the surface layer) indicates that the clusters or aggregates are, on average, randomly oriented disks. But the data from toluene suggest that the disks, although random, still form loosely correlated face-to-face stacks separated by a distance roughly equivalent to the height of the disk itself. Furthermore, the data suggest strongly that the disks are also correlated end-to-end.

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